IONIZED POLYCYCLIC AROMATIC HYDROCARBONS AND THE DIFFUSE INTERSTELLAR BANDS

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ABSTRACT

A good case has recently been made that the unidentified infrared emission features arise from positively charged, partially hydrogenated polycyclic aromatic hydrocarbons (PAHs). In this *Letter*, we suggest that these exceedingly stable ions are also the carriers of the diffuse interstellar bands. Although a large variety of PAH isomers is possible, the more condensed forms are substantially more stable than the less condensed forms and are expected to be dominant in the harsh interstellar environment. While neutral PAHs do not absorb in the visible, their ionized counterparts do. Because of their low ionization potential, a substantial fraction of the interstellar PAHs will be ionized. Visible spectra of the most stable PAH cations isolated in glasses are compared directly to the interstellar band spectra. Although the laboratory spectra are on an extremely compressed scale and solid state shifts are present, the comparison is favorable. Since little information is available concerning the spectroscopic properties of these species in the gas phase, a considerable amount of laboratory and theoretical work is called for to test this hypothesis.

Subject headings: infrared: spectra — interstellar: matter — interstellar: molecules

I. INTRODUCTION

Understanding the origin of the many diffuse interstellar absorption bands found in the visible has been elusive since their discovery more than 50 yr ago (Merrill 1934). Excellent reviews of the problem, including a thorough discussion of possible carriers (dust or gas phase), have been written by Herbig (1975) and Smith, Snow, and York (1977). The strength of the diffuse interstellar bands (DIBs) correlates reasonably well with the visible extinction due to interstellar dust. However, the nearly symmetric profile, the absence of emission wings, and the lack of polarization variation across some of the bands argues against an origin in large dust grains (radius ≈ 1000 Å: Herbig 1975; Martin and Angel 1974). An origin in smaller grains (~ 100 Å) also seems to be ruled out, since the DIBs are poorly correlated with the UV extinction ($\lambda \leq$ 1500 Å; Seab and Snow 1984). Because of these difficulties, attention has shifted from an origin in the bulk of the grain to molecules on the surface of small grains (Federman, Kumar, and Vanden Bout 1984; Seab and Snow 1984). For example, Duley and McCullough (1977) have suggested that polyatomic molecular ions adsorbed on grain surfaces could be responsible for some of the diffuse bands. Despite the fact that most gas phase molecules cannot survive the harsh interstellar environment long enough to maintain the abundance required to account for the DIBs, a general case has been made that vibronic transitions in complex molecules could be responsible (Smith, Snow, and York 1977; Douglas 1977). Linear, planar, or ring molecules can possess band profiles similar to those

observed (Danks and Lambert 1976). In this *Letter* the possibility that a collection of ionized, very stable, complex, gas phase molecules known as polycyclic aromatic hydrocarbons (PAHs) could be the carrier of the DIBs is discussed. In effect this is an extension of the original speculation by Donn (1968) that radical sidechains on neutral PAHs might be the carriers.

Many different types of celestial objects show IR emission features, which have recently been attributed to polycyclic aromatic hydrocarbons (Duley and Williams 1981; Leger and Puget 1984; Allamandola, Tielens, and Barker 1985). This assignment is based on a spectroscopic analysis of these features. In particular the 3.3 μm and 6.2 μm emission features are highly characteristic of fundamental vibrations in aromatic rings (Cyvin *et al.* 1982). Comparison of the observed 6.2 and 7.7 μm bands with the laboratory measured Raman spectrum of a collection of carbon-based particulates shows very good agreement, supporting this identification (Allamandola, Tielens, and Barker 1985). From a comparison of the observed ratio of the 3.3 to 11.3 μm emission bands with model calculations of the IR fluorescence of vibrationally excited PAHs, the average number of carbon atoms per PAH is estimated to be about 20.

II. STABILITY

The presence of the IR emission bands in a wide variety of objects indicates the existence of PAHs in the interstellar medium, even outside dense molecular clouds and circumstellar shells. Interstellar PAHs are probably formed in the carbon-rich outflow from planetary nebulae and carbon-rich Miras. Figure 1 illustrates the first steps in the high-temperature carbon polymerization route which is thermodynamically most favorable (Stein 1978). Note that the pericondensed

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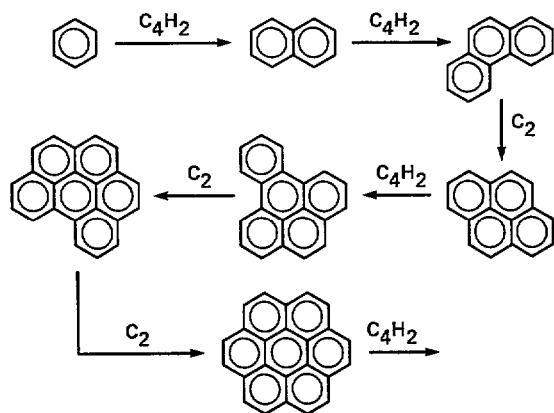[4] National Research Council Associate.

FIG. 1.—First six members of the most thermodynamically favorable high-temperature PAH polymerization route (Stein 1978). Successive members of this series are formed by adding two or four carbon atoms at a time, the number required to complete an additional fused aromatic ring. Note that C_2 and C_4H_2 refer only to the number and type of atoms added in each step and do not refer to specific chemical species or mechanisms. Similarly, the circles here and in Fig. 2 indicate planarity and overall electron delocalization.

PAHs (i.e., some carbon atoms shared by more than two rings) are substantially more stable than the catacondensed PAHs (i.e., each carbon atom shared by at most two rings). The pericondensed PAHs are thermodynamically favored because this form permits electron delocalization to a larger extent than the catacondensed species.

The distribution of PAHs ejected by carbon-rich objects will be further modified by physical processes in the interstellar medium, such as photodissociation, which will weed out the less condensed, less stable forms. The carbon skeleton of pericondensed PAHs is very stable (Clar 1972). Absorption of an UV photon can produce stable ions, induce the loss of an H atom, or rearrange the skeleton to a more stable form. However, little or no fragmentation of the carbon skeleton is expected (Turro 1978). Note that the carbon skeleton will not fragment when one bond is broken. It will rather rearrange its geometry (photoisomerization) within a few torsional periods (10^{-12} s). This will convert the less stable catacondensed PAHs into their more stable pericondensed isomers. In order to remove a carbon atom or fragment an aromatic ring, two three-electron bonds have to be broken (~ 11.5 eV; Benson 1965). Thus, in the diffuse interstellar medium, almost all of the absorbed UV photon energy has to be localized simultaneously in these two bonds. Representing the molecule by a collection of oscillators of equal frequency, the probability of this event's occurring in a highly vibrationally excited PAH can be crudely estimated from unimolecular rate theory (cf. Dalgarno 1975) to be extremely small, even for a 20 atom PAH (i.e., lifetime $\geq 10^{16}$ s). Given the short radiative relaxation time scale (0.1 s) and the long time scale for UV photon absorption (10^9 s), photodestruction of the more stable PAHs in the diffuse interstellar medium is unimportant, and their lifetimes are expected to be comparable to that of small carbon grains.

III. VISIBLE ABSORPTION SPECTRA OF POLYCYCLIC AROMATIC HYDROCARBONS

For neutral PAHs, the wavelength of the lowest energy electronic transition will depend on the length of the long axis

of the molecule (Platt 1956). In essence this is because a long chain of aromatic rings has more closely spaced energy levels than a short chain and therefore absorbs at longer wavelengths (cf. a particle in a box). For coronene ($C_{24}H_{12}$) the absorption starts at about 3600 Å (Birks 1970). The smallest neutral pericondensed PAH that will absorb at the blue end of the visible is circumcoronene ($C_{54}H_{18}$). In order to absorb throughout the visible, substantially larger PAHs are needed. The abundance of such large PAHs is, however, expected to be low as deduced from the ratio of the 3.3 to 11.3 μm IR emission features (Allamandola, Tielens, and Barker 1985).

However, because of their low ionization potential (~ 6 eV), a large fraction of the PAHs are expected to be ionized in the interstellar medium, except in dense clouds (Allamandola, Tielens, and Barker 1985). Ionized aromatic molecules have strong absorption bands in the visible due to the presence of an unpaired electron. Visible absorption spectra of several PAH cations, suspended in alkali halide or freon matrices, are shown in Figure 2 (Shida and Iwata 1973). The spectra of these particular species are selected out of the many cation spectra reported by Shida and Iwata (1973) because of their unusual stability, as indicated by their presence in the carbon polymerization route (Fig. 1). Unfortunately, visible spectra of larger condensed PAH cations do not seem to be available in the literature. Also, the observed interstellar IR spectra indicate that the PAHs are only partially hydrogenated (Duley and Williams 1981). Because such radicals might also absorb in the visible, partial hydrogenation may influence the vibronic pattern of the cations.

IV. DISCUSSION

A schematic representation of the spectrum of the DIBs is compared to the laboratory spectra in Figure 2 (Herbig 1975; Sanner, Snell, and Vanden Bout 1978). Because of the compressed frequency scale of the laboratory data available in the literature, the equivalent width of the DIBs, rather than the peak optical depth, has been used in preparing this figure. For that reason the broader DIBs (e.g., $\lambda = 4430$ Å) tend to dominate. In this comparison it should be borne in mind that the highly polarizable matrices, used to suspend the cations in the laboratory, will induce a redshift of the absorption bands with respect to the gas phase. For example, in naphthalene, depending on the states involved, this shift can be as large as 2000 cm^{-1} (Andrews, Kelsall, and Blankenship 1982). To compensate for this shift, the DIB spectrum frame is redshifted by 1500 cm^{-1}. In view of this large matrix shift and the small scale of the laboratory data, only tentative conclusions can be made at this stage. It seems, nonetheless, that a collection of PAH cations might be able to account for the diffuse interstellar bands. The pericondensed cations could account for the stronger blue DIBs, such as those at 4430 Å and 4880 Å, while the smaller catacondensed PAHs exhibit a richer pattern of red vibronic absorption bands, remarkably similar to that of the DIBs. It should be emphasized that the selection of spectra plays an essential role in this comparison. In particular, if all of the possible PAH isomers had been included then the PAH spectrum would have shown far too many vibronic absorption bands in comparison to the DIBs. The compressed frequency scale of the cation spectra is, of course, very forgiving of frequency mismatches and caution concerning the conclusions drawn is warranted. Nevertheless,
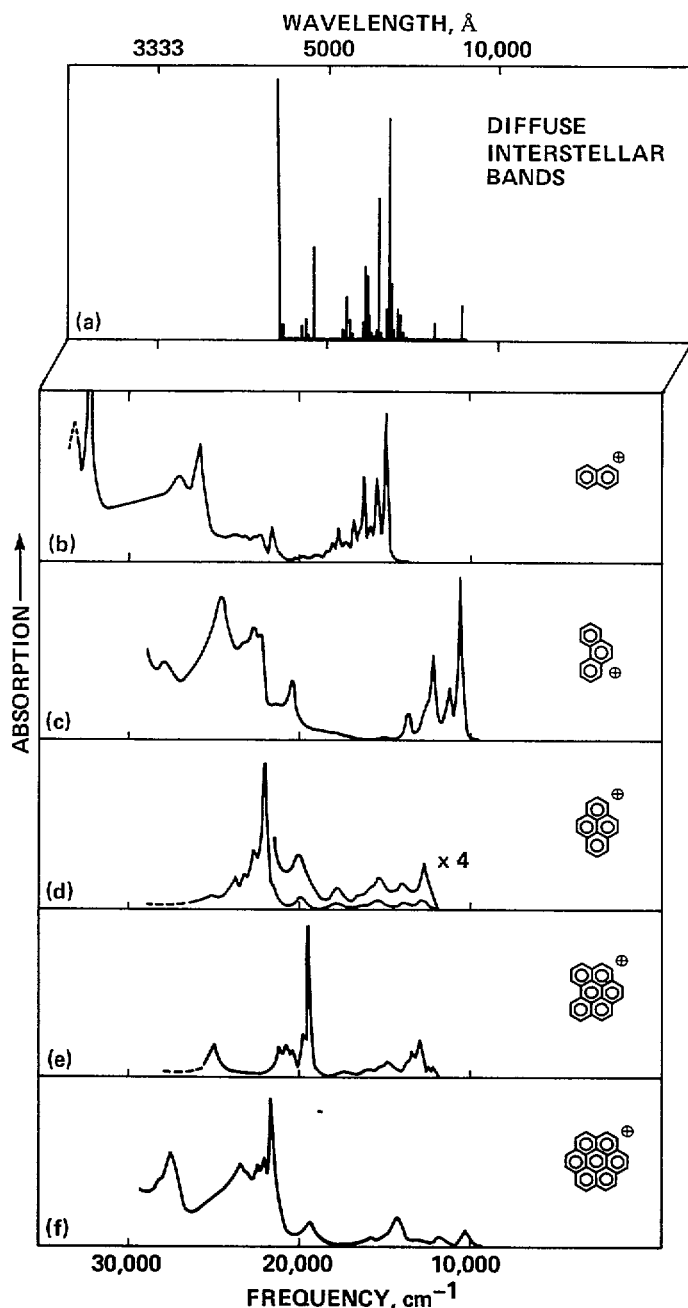
FIG. 2.—(a) Schematic bar representation of the DIB spectrum (Herbig 1975; Sanner et al. 1978). The length of each bar represents the equivalent width. This frame is redshifted by 1500 cm^{-1} with respect to the frames below to compensate for the red matrix shift inherent in the cation spectra. (b)–(f) Visible absorption spectra of 5 PAH cations isolated in alkali halide or freon matrices (Shida and Iwata 1973). These cations, selected on the basis of their thermodynamic stability (Fig. 1) are of (b) naphthalene ($C_{10}H_8$), (c) phenanthrene ($C_{14}H_{10}$), (d) pyrene ($C_{16}H_{10}$), (e) 1,12-benzperylene ($C_{22}H_{12}$), and (f) coronene ($C_{24}H_{12}$).

we feel that the agreement between the DIBs and the vibronic absorption spectra of the most thermodynamically favored stable PAH cations is striking enough to justify further serious consideration.

Because oscillator strengths for the vibronic transitions of PAH cations have not yet been measured, it is difficult to estimate the PAH abundances required to explain the DIBs.

However, in view of the short interchange time between molecular clouds and the diffuse interstellar medium ($\approx 3 \times 10^7$ yr) compared to the long interchange time between the interstellar medium and stars ($\sim 10^9$ yr), the PAH abundance in the interstellar medium is expected to be similar to that derived from IR observations for molecular clouds (2×10^{-7} with respect to H; Allamandola, Tielens, and Barker 1985). Assuming that the same species are responsible for both the IR emission bands and the DIBs, an oscillator strength of 0.1 summed over all visible vibronic bands is required in order to account for the strength of the DIBs. This is a reasonable value for the absorption strength of vibronic bands in neutral PAHs and, by inference, for ionized PAHs as well (Birks 1970). At this stage it is difficult to decide whether the depth of the strong DIBs, such as 4430 Å, is caused by a large oscillator strength or by a high abundance of the specific cation involved. It is also possible that it is due to the presence of more than one cation absorbing at the same frequency (i.e., coronene and pyrene for 4430 Å; cf. Fig. 2).

In addition to the visible bands, many of the PAH cations have very broad UV absorption bands, as do their neutral counterparts. However, in the interstellar collection of PAHs, these may be difficult to detect, because they will blend together. Detection may also be hampered by the uncertain baseline and the large number of ultraviolet stellar absorption lines (Seab and Snow 1984).

Because of the interactions between the host and guest species in the alkali halide or freon matrices, the vibronic bands are considerably broadened and perturbed in the laboratory data. Furthermore, the molecules are not free to rotate. This precludes a direct comparison of the laboratory profiles with the profiles of the diffuse interstellar bands. In the gas phase, the profile of each vibronic absorption band is determined by the rotational structure. The band profiles expected are suggestive of some diffuse band contours (Danks and Lambert 1976; van der Zwet and Allamandola 1985). Rapid electronic relaxation, particularly in the higher electronic states, can also cause line broadening (diffuseness: Byrne and Ross 1971; Jortner, Rice, and Hochstrasser 1969).

One of the objections to attributing the DIBs to gas phase molecules has been the absence of correlated visible diffuse emission bands (Smith, Snow, and York 1977). Indeed, neutral PAHs generally fluoresce in the near-ultraviolet or visible with a quantum yield of about 20% (Birks 1970). This fluorescence usually occurs from the lowest excited electronic state having the same multiplicity as the ground electronic state (Kasha 1950). Ionized PAHs, however, do not seem to fluoresce in the visible. For example, the lowest transition of the naphthalene cation is not electric dipole allowed, thus explaining the absence of visible fluorescence (Andrews, Kelsall, and Blankenship 1982). The lowest electronic transition of the coronene cation, which is electric dipole allowed, is at a wavelength longer than 1 μm (Hoijtink 1959). Any fluorescence would therefore be expected to be in the near-infrared. Furthermore, radiationless transitions can play an important role in large molecules (Byrne and Ross 1971; Jortner, Rice, and Hochstrasser 1969). For these reasons the ionized PAHs should appear only in absorption in the visible, which is consistent with the behavior of the diffuse bands. We note that fluorescence from low-lying electronic states of PAH cations may contribute to the infrared continuum radiation observed in reflection nebulae (Sellgren, Werner, and Dinerstein 1983).

In conclusion, ionized PAHs, generally present in the interstellar medium as evidenced by the IR emission bands, may also be able to account for the diffuse interstellar bands. Spectra of PAH cations taken in molecular beam expansion experiments, where the isolated, cold conditions more closely approximate those in the interstellar medium, will allow a direct comparison of PAH cation and DIB line profiles and wavelengths. This may ultimately lead to the identification of the specific interstellar PAH cations involved.

After this work was completed we received a preprint by Leger and d'Hendecourt, which deals with the same problem.

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